

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
15 February 2001 (15.02.2001)

PCT

(10) International Publication Number
WO 01/10795 A1

(51) International Patent Classification⁷: C04B 41/89

9865 E. Windrose Drive, Scottsdale, AZ 85260 (US). RAY-BOULD, Derek; 2 Horizon Drive, Denville, NJ 07834 (US).

(21) International Application Number: PCT/US00/21788

(22) International Filing Date: 10 August 2000 (10.08.2000)

(74) Agents: CRISS, H. Roger et al.; AlliedSignal Inc., 101 Columbia Avenue, P.O. Box 2245, Morristown, NJ 07960 (US).

(25) Filing Language: English

(26) Publication Language: English

(81) Designated State (national): JP.

(30) Priority Data:
09/371,826 11 August 1999 (11.08.1999) US

(84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

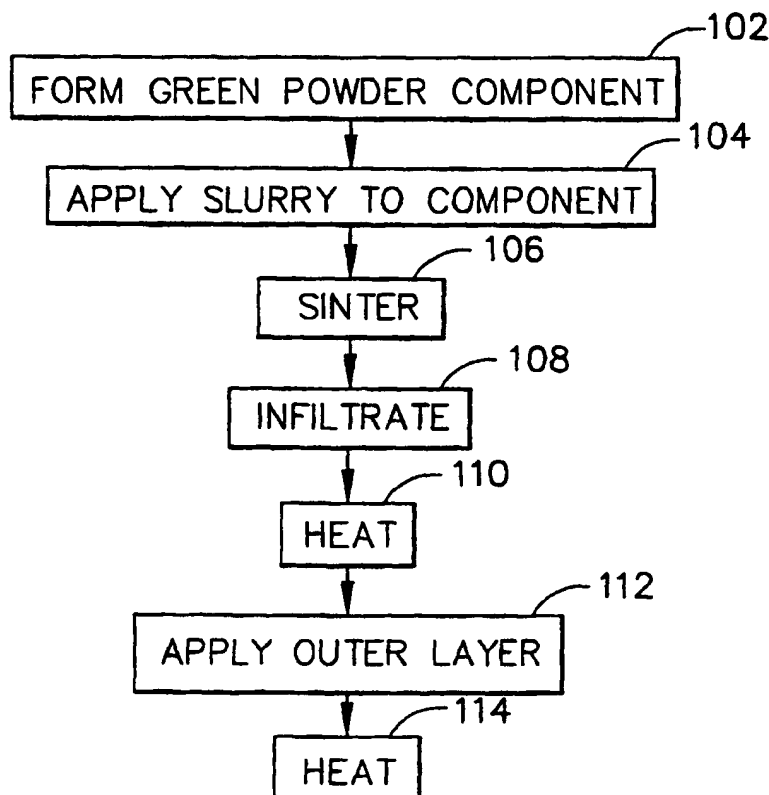
(71) Applicant: ALLIEDSIGNAL INC. [US/US]; 101 Columbia Avenue, P.O. Box 2245, Morristown, NJ 07960 (US).

Published:
— With international search report.

(72) Inventors: LI, Chien-Wei; 11 Crescent Road, Livingston, NJ 07039 (US). STRANGMAN, Thomas, Edward; 7632 N. 22nd Street, Phoenix, AZ 85020 (US). ORTIZ, Milton;

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: SILICON NITRIDE COMPONENTS WITH PROTECTIVE COATING



(57) Abstract: A turbomachine component includes a silicon nitride substrate and a multilayer coating bonded to the substrate. The coating includes an interlayer of porous fibrous silicon nitride having a density of between 85-98 %. The coating also includes an outer layer formed of an oxide compound, preferably tantalum oxide, that is applied by Electron Beam-Physical Vapor Deposition. The combination of the silicon nitride interlayer and tantalum oxide outer layer serves to protect the substrate from the adverse affects of oxidation, impact by foreign objects and extreme operating temperatures.

SILICON NITRIDE COMPONENTS WITH PROTECTIVE COATING

BACKGROUND OF THE INVENTION

The present invention relates to turbomachines and similar apparatus having
5 components formed of silicon nitride ceramic material. More specifically, the present invention relates to protective coatings for such components.

Certain components of gas turbines are often coated or even formed from silicon nitride ceramic material to counteract the adverse effects of oxidation and water vapor that can occur at extremely high operating temperatures. Such
10 components may include the turbine blades, rotors, and nozzles. By forming turbomachine components of silicon nitride, it becomes possible to operate the turbomachines with improved efficiency and reduced pollutant emissions at temperatures above 1200°C. However, for operating temperatures approaching 1480°C, even silicon nitride blades, rotors and nozzles can be adversely effected by
15 oxidation and water vapor present in the flow stream.

It would be desirable to protect the silicon nitride substrates of the components in a way that reduces oxidation and also provides a thermal barrier. Partially stabilized zirconia (PSZ) has been employed as a thermal barrier coating for components made of superalloy. However there is a significant mismatch in the
20 thermal expansion coefficient between zirconia ($\sim 10 \times 10^{-6}$) and silicon nitride ($\sim 3.5 \times 10^{-6}$). Because of this thermal mismatch, thermal cycling can easily debond the coating from the silicon nitride substrate. In addition, zirconia is a fast ionic conductor for oxygen and a poor oxidation barrier.

Though silicon nitride blades and nozzles have exhibited excellent mechanical
25 and thermal properties, even when employed in flow streams at temperatures in excess of 1200°C, silicon nitride is not without its drawbacks. One drawback is impact failure, generally caused by foreign objects such as carbon or metallic particles encountered in the turbine engine flow stream. Because of this drawback, there has been some reluctance to even employ silicon nitride turbine components.

To overcome the low impact resistance problem, it would be desirable to somehow strengthen the silicon nitride component substrate to enhance the impact resistance without adversely affecting the thermal properties of the substrate. It would also be desirable to minimize overall component weight.

5

SUMMARY OF THE INVENTION

The present invention is directed to machine components having substrates formed of silicon nitride. The substrate is coated with an interlayer of silicon nitride having a porous fibrous surface with a density in the range of about 85-98%. An
10 outer layer of tantalum oxide or similar compound having a thermal coefficient in the range of $2.5 \sim 5.0 \times 10^{-6}$ may cover the interlayer.

Another aspect of the invention is directed to a process for coating turbomachine components with a multi-layered coating. The method includes the step brushing or spraying an interlayer of a silicon nitride powder slurry onto the
15 component substrate. The slurry and substrate composition are then sintered at a temperature in excess of 1700°C to grow porous fibers on the composition. The composition is then infiltrated with a precursor solution which may include a pre-ceramic polymer. The composition is heated to convert the precursor into a matrix surrounding the fibrous silicon nitride layer in order to protect the component during
20 operation. The interlayer has a density in the range of 90-98%.

An outer layer of tantalum oxide may be applied to the outer surface of the interlayer by Electron Beam-Physical Vapor Deposition.

BRIEF DESCRIPTION OF THE DRAWINGS

25 Figure 1 is an illustration of a gas turbine engine having components formed in accordance with the present invention;

Figure 2 is an illustration an engine component formed in accordance with the present invention; and

Figure 3 is a flowchart of a method of coating a silicon nitride substrate.

DETAILED DESCRIPTION OF THE INVENTION

Referring to FIG. 1, a gas turbine engine 10 includes, in serial flow relation from inlet to exhaust, an inlet frame 14, a two stage low pressure compressor ("LPC") or fan 16, a three stage high pressure compressor ("HPC") 18 and a combustor 20. In addition, the engine 10 includes a single stage high pressure turbine ("HPT") 22, a two stage low pressure turbine ("LPT") 24, a turbine frame 26, and an exhaust nozzle 28. Each of the turbines 22 and 24 includes a plurality of stationary turbine vanes 30 and a plurality of rotating turbine blades 32. The design of the turbine engine 10, in itself, is discussed to better understand the components that make up the present invention. During operation of the turbine engine 10, a stream of air S enters the engine assembly 10 through inlet 14, travels through the open interior 27 of the engine assembly 10 and exits through outlet nozzle 28. As the stream S passes through the engine 10, high temperature combustion effluent gases mix with the stream S as it passes through interior 27 before being expelled by nozzle 28.

The turbine vanes 30 and 32 may be formed of silicon nitride. However, if the stream S achieves temperatures of about 1480°C, as may well occur during operation of the turbine engine 10, uncoated silicon nitride components would be adversely affected by the excessive thermal temperatures as well as by oxidation from any water vapor present. In addition, the uncoated silicon nitride can be sensitive to impact by foreign particles.

As shown in FIG. 2, a multi-layer coating 40, formed in accordance with the present invention, is applied to an outer substrate 41 of a turbomachine component such as a turbine vane 32. The substrate of turbine vane 32 is made of a dense silicon nitride having density of greater than 99.3%. The multi-layer coating 40 includes an interlayer 42 directly applied to the silicon nitride substrate 41 and an outer layer 44 applied to interlayer 42.

Preferably, the interlayer 42 comprises a fibrous composite layer of beta silicon nitride. The interlayer 42 is porous and has a whisker-like microstructure

exhibiting high impact resistance due to its high fracture toughness and ability to absorb impact energy. The interlayer 42 enjoys good adhesive properties, assuring that the outer layer 44 will permanently bond to the interlayer 42. The interlayer 42 has a thickness in the range of about 0.5 mil to 20.0 mil and, preferably, from about
5 1.0 mil to 10.0 mil. The density of the fibrous silicon nitride making up the interlayer 42 is about 85-98%. That is, the porosity of the interlayer 42 is between 2-15%. This high density is achieved by repeated infiltration of the interlayer 42 as will be explained. Because of the repeated infiltration step, the density of the interlayer 42 can reach 90-98%.

10 The outer layer 44 envelopes the interlayer 42 and functions as a thermal barrier. The outer layer 44 is chosen to have a thermal expansion coefficient that approximates that of silicon nitride, or $\sim 3.5 \times 10^{-6}$. Preferably, the outer layer 44 is formed of dense tantalum oxide, Ta_2O_5 . Alternatively, oxide compounds having a thermal match, i.e. in a range of $2.5\sim 5.0 \times 10^{-6}$ may be substituted for the Tantalum.
15 Such compounds may include the oxides of hafnium ("Hf"), niobium ("Nb"), titanium ("Ti"), nickel ("Ni"), tungsten ("W"), aluminum ("Al"), magnesium ("Mg"), strontium ("Sr"), or zirconium ("Zr"). An outer layer 44 of tantalum oxide has a thickness that ranges from about 0.2 to 20.0 mil and, preferably from about 1.0 to 10.0 mil.

20 Reference is now made of FIG. 3, which illustrates a method of manufacturing turbomachine components such as nozzles 28 and vanes 30, 32 of silicon nitride. Preferably, the components are manufactured by the powder metallurgy process. Such a process includes forming green powder compacts of the various components to be manufactured (step 102). The interlayer 42 is then formed when a silicon nitride
25 powder slurry is sprayed or brushed 104 onto the substrate 41 of the green components (step 104). The powder in the slurry includes silicon nitride and certain additives.

The additives directly affect the sintering of the silicon nitride and may consist of rare earth oxides, nitrides and oxides/nitrides of Al, Mg, Sr or the like. Powders

that serve to hinder sintering of silicon nitride, such as BN, may also be added to control the amount of shrinkage of the interlayer 42 applied during the manufacturing process. Because the interlayer 42 has a lower green density than the underlying green silicon nitride components, the interlayer 42, once applied to substrate 41, may shrink excessively compared to the substrate 41 if the amount of the sintering aid in the slurry is excessive. This, in turn, results in detachment of the interlayer 42 from the substrate 41. Alternatively, if the sintering aids are not included, or an insufficient amount is present, interlayer 42 would not shrink a sufficient amount during sintering to substrate 41, causing interlayer 42 to detach from substrate 41. Preferably, the sintering aids are in the range of 2-20wt% of the total amount present.

Once the interlayer 42 is sprayed or brushed onto the substrate 41 during step 104, the turbomachine components along with the interlayer 42 undergo a reaction or sintering step 106 at a temperature in excess of 1700°C (step 106). This step causes beta silicon nitride fibers to form and grow in both the substrate and the interlayer 42 until they reach a length which may exceed 100 microns. The use of a combination liquid and vapor phase process along with the open space defined by substrate 41 ensures that growth of the fibers will be fast and uninhabited. The silicon nitride fibers form whiskers that extend between substrate 41 and the interlayer 42, binding the interlayer to the substrate 41.

Once the substrate 41 and interlayer 42 have been sintered during step 106, a solution precursor is infiltrated into the porous, fibrous surface of interlayer 42 by dipping the substrate 41 and attached interlayer 42 into a liquid solution (step 108). The liquid infiltration solution can be a pre-ceramic polymer which converts to a silicon-nitrogen-carbon glass after pyrolysis, or a pre-ceramic polymer pre-mixed with filler powders. For example, a commercially available liquid polyureasilazane polymer with the addition of 0.5wt% peroxide may be utilized as initiator. The filler powder may be an oxide, carbide, nitride or metal. The solution is not limited to a pre-ceramic polymer. Filler powders may be mixed with other inorganic liquids for infiltration.

The infiltration step 108 is preferably conducted under vacuum to assist in liquid penetration of the interlayer 42. During the next step 110, pyrolysis occurs when a stream of Ar or nitrogen is applied to the component and attached interlayer as they are heated to a temperature of between 500-2000°C in graphite furnace for approximately thirty (30) minutes. The heating serves to convert the precursor into crystalline or amorphous ceramics that form a matrix surrounding the fibrous material. When a ceramic precursor is utilized in the infiltration step, oxide, carbide, nitride or their combination will be present after the pyrolysis treatment is completed. It may include compounds based on S-N-C-X where X represents other ions such as B.

The infiltration and pyrolysis steps 108 and 110 may be repeated as many times as required to form a dense coating of Si-N-C material reinforced by fibrous beta silicon nitride. The attached interlayer 42 protects substrate 41 against oxidation, it is damage resistant and it functions as a thermal barrier coating. The interlayer 42 also provides a bond coating for the outer layer 44.

The outer layer 44 may comprise a ceramic powder, preferably tantalum oxide, which can be applied to the interlayer 42 by a variety of known methods including Plasma Spray Coating, Electron Beam PVD, and chemical vapor deposition on silicon nitride. In place of tantalum oxide, oxide compounds with a thermal expansion coefficient of between $2.5 \sim 5.0 \times 10^{-6}$ including Hf, Nb, Ti, Ni, W, Al, Mg, Sr, Zr or the like may be employed. Fillers from oxide, carbide, nitride also may be incorporated into the outer layer 44 as desired.

In order to apply the outer coating 44 of tantalum oxide to the interlayer 42 (already bonded to the silicon nitride substrate 41), a plasma sprayer assembly may be employed. The ceramic tantalum oxide powder is fed into a high velocity, high temperature plasma flow which is directed against the silicon nitride substrate 41 and attached interlayer 42 in step 112. Due to the high plasma temperature, the ceramic powder becomes molten, and subsequently is quenched and solidified on the cooler silicon nitride interlayer 42. The silicon nitride component with attached coating 40

may be heated to about 1000°C during step 114, to improve bonding between the plasma sprayed outer layer 44 and interlayer 42 of coating 44.

In an alternative method of accomplishing step 112, an Electron Beam-Physical vapor Deposition (EB-PVD) process may be employed. EB-PVD offers
5 several significant benefits over that of a chemical vapor deposition (CVD) coating process. The coating rate using EB-PVD is much faster than that of CVD, and the bonding created by the EB-PVD process to a silicon nitride substrate is much stronger. In the EB-PVD process a high-energy electron beam is focused on an ingot of the material to be deposited (e.g., tantalum oxide). The electron bombardment
10 results in high local heating on the coating material, which material evaporates at the atomic level and condenses on the component. A chemical bond is formed between the outer layer 44 and the interlayer 42. The substrate 41 and attached interlayer 42 are preferably preheated to improve bonding with the outer layer 44.

While the interlayer 42 and the outer layer 44 work together to maximize
15 protection of component substrate 41, the outer layer 44 may be applied directly onto the substrate 41. To coat the silicon nitride substrate 41 directly with tantalum oxide, either pure tantalum or a tantalum oxide ingot is used with the EB-PVD process. Whether applying the outer layer 44 to the inner layer 42 or directly to substrate 41, oxygen is bled into the EB-PVD system during the evaporation of the pure tantalum
20 or tantalum oxide ingot, to react with the tantalum-containing vapor to form tantalum oxide. If the outer layer 44 is applied directly to the substrate 41, the outer surface of the substrate 41 may be roughened to increase the bond with the outer layer 44.

The coating 40 may include one or more additional layers applied to outer layer 44 to provide further thermal insulation and impact resistance to foreign objects
25 striking the component during operation of the turbomachine (see FIG. 1 at 46). For example, a layer of zirconia may be applied to the outer layer 44 to increase its ability to function as a thermal barrier.

This invention is further described, although not limited by the following examples:

EXAMPLE 1

A silicon nitride aqueous slurry slip is prepared by ball milling for 22 hours. The aqueous slurry includes a silicon nitride composition consisting of 82 wt% Si_3N_4 ,
5 4wt% Y_2O_3 , 3wt% La_2O_3 , 1 wt% SrO and 10wt% SiC . To improve the slip quality, 0.5% Darven C Standard slipcasting is performed using the slurry to form a green piece of $\sim 2.2'' \times 2.2'' \times 0.7''$. A portion of the slurry is further diluted to 50-60% solid loading by adding water, and the diluted slurry is applied by a commercial spray gun on the slipcast block. After the spray-coated block dries, it is loaded onto a graphite
10 crucible and sintered in a graphite furnace at a temperature of about 1850°C for about two hours under 100 psi nitrogen, 1950°C for about three hours under 170 psi nitrogen and about 2025°C for about two hours under 400 psi nitrogen. After sintering, the block is at about 99.5% of its theoretical density, and a coherent top layer consisting of a layer of fibrous beta silicon nitride is formed.

15 A commercially available liquid polyureasilazane polymer with 0.5wt% peroxide as initiator is prepared. The sintered silicon nitride with fibrous top coating is immersed into the liquid polymer, and vacuum is applied to infiltrate the polymer into the porous fibrous layer. After the infiltration step is completed, the coated ceramic is pyrolyzed in a graphite furnace under flowing nitrogen for 30 minutes at
20 1000°C . After pyrolysis is completed, the polymer is converted into a Si-N-C material. After repeated polymer infiltration and pyrolysis is completed, a dense coating of Si-N-C material reinforced by the fibrous beta silicon nitride is formed. A block is machined into coupons of $\sim 2'' \times 0.12'' \times 0.16''$ to undergo EB-PVD coating of tantalum oxide. The coupons are degreased and then loaded into an EB-PVD system.
25 The coupons are mounted to have the coated silicon nitride interlayer facing a tantalum ingot where a Ta vapor would be generated from bombardment by an electron beam. During the coating step, the coupons are heated to $\sim 1000^\circ\text{C}$ to enhance bonding, and oxygen was bled into the system to form a tantalum oxide outer layer bonded to the silicon nitride interlayer.

EXAMPLE 2

A coating of tantalum oxide is applied to coupon of ~2" x 1" x 0.12" of silicon nitride substrate by a plasma spray process wherein a commercially available tantalum
5 oxide ceramic powder was used as feedstock. The coupon is degreased, and then preheated to ~1000°C by either a torch or a furnace. The tantalum oxide powder is then fed into a high velocity, high temperature plasma flow. The ceramic powder becomes molten and subsequently is quenched and solidified onto the fibrous silicon nitride coupon.

10

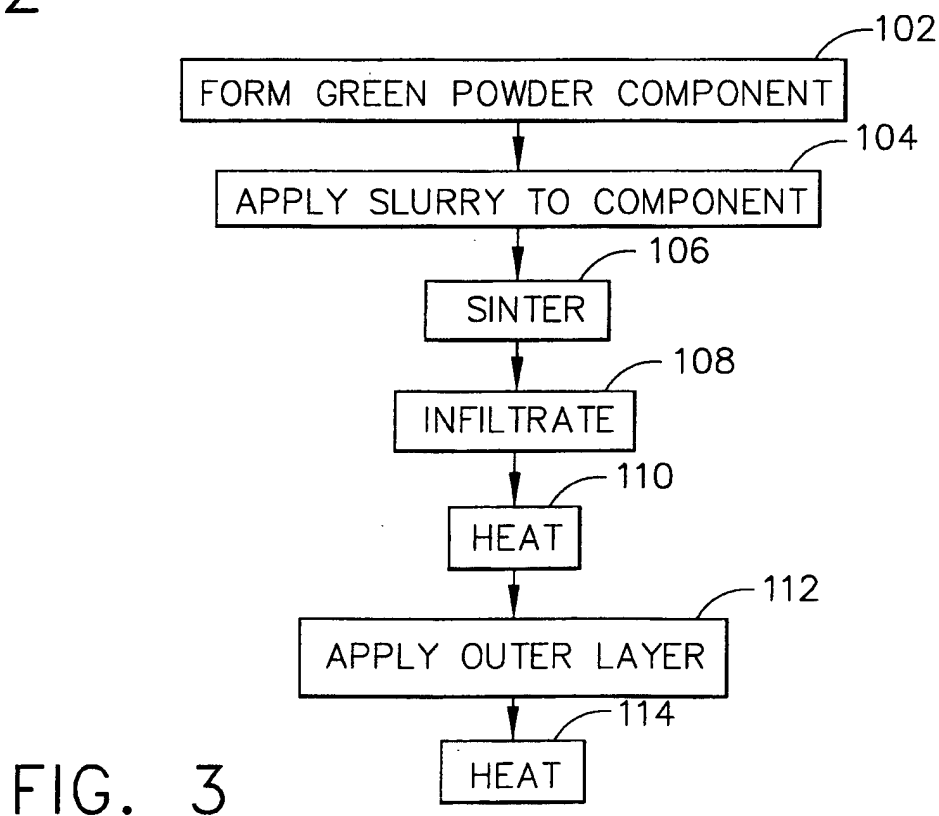
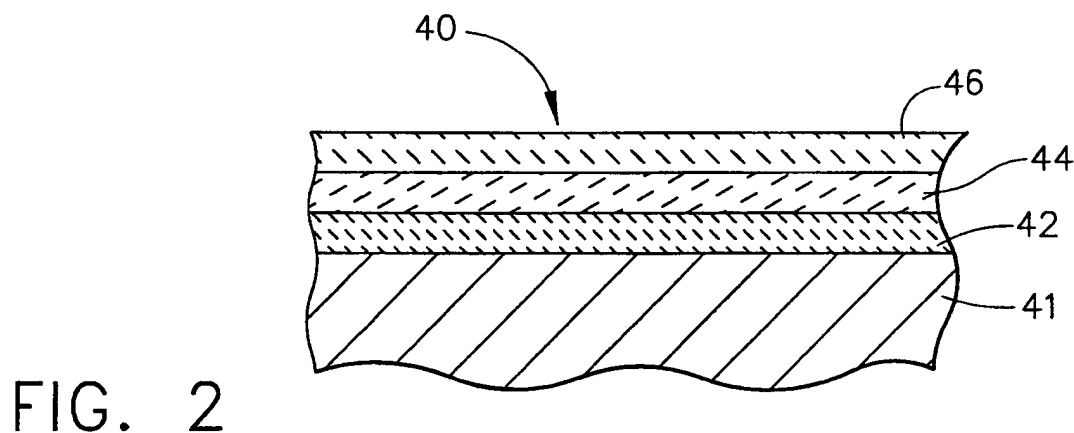
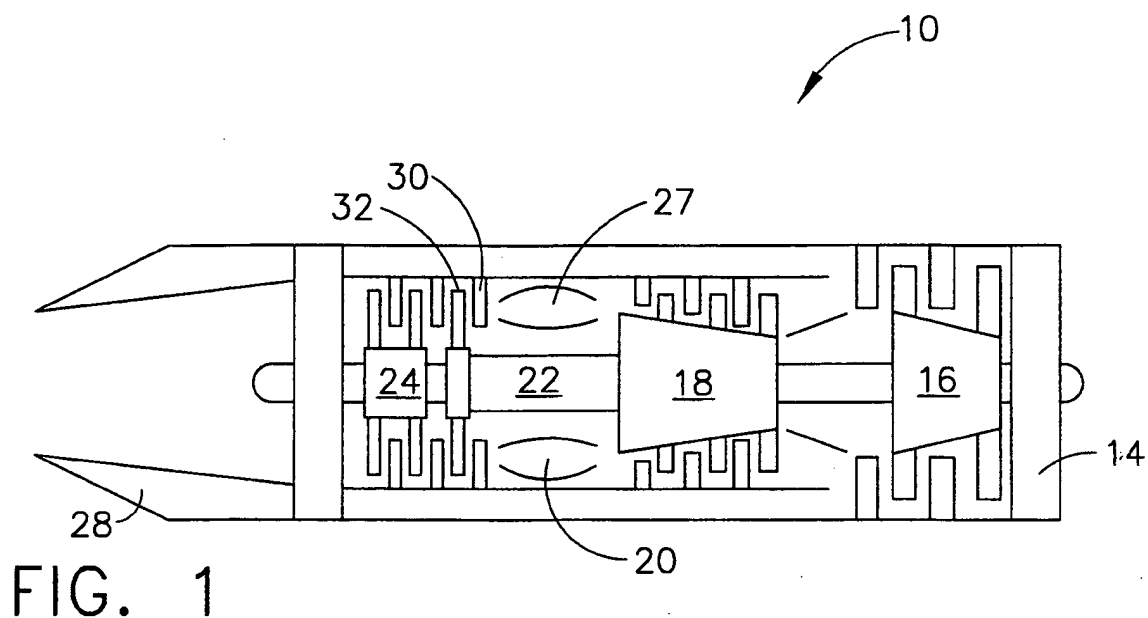
Turbine engine components other than blades, nozzles and rotors may be coated in accordance with the present invention. For example, turbine shrouds may be coated in accordance with the present invention. Moreover, the present invention is not limited to use in turbine engines.

15 Although the present invention has been described above with reference to specific embodiments, it is not so limited. Instead, the present invention is constructed according to the claims that follow.

WHAT IS CLAIMED IS:

1. A method of coating a silicon nitride substrate, comprising the steps of:
applying a silicon nitride powder slurry onto the silicon nitride substrate
(104);
sintering the applied slurry to produce a porous beta silicon nitride layer
5 having whisker fibers extending into the substrate for binding the layer to the
substrate (106);
infiltrating the porous outer surface of the composition with a precursor
solution (108); and
heating the composition to convert the precursor solution into a matrix
10 surrounding the fibrous material (110).
2. The coating method of Claim 1, wherein the infiltrating step includes
dipping the substrate into a liquid solution formed of a pre-ceramic polymer.
- 5 3. The coating method of Claim 1, wherein silicon nitride powder slurry and
substrate composition are sintered at a temperature in excess of 1700°C.
4. The coating method of Claim 1, further comprising the step of coating the
fibrous silicon nitride and surrounding matrix with an oxide compound having a
10 thermal expansion coefficient in the range of $2.5\sim 5.0 \times 10^{-6}$ (112).
5. The coating method of Claim 4, wherein the oxide compound is applied by
Electron Beam-Physical Vapor Deposition.
- 15 6. The coating method of Claim 4, wherein the oxide compound is selected
from the group consisting of Ta, Hf, Nb, Ti, Ni, W, Al, Mg, Sr, and Zr.

1/1



BEST AVAILABLE COPY

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C04B41/89

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C04B F01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 01, 28 February 1995 (1995-02-28) & JP 06 287095 A (TOSHIBA CORP), 11 October 1994 (1994-10-11) abstract	1



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

8 November 2000

Date of mailing of the international search report

16/11/2000

Name and mailing address of the ISA

 European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3018

Authorized officer

Rosenberger, J

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 06287095 A	11-10-1994	NONE	